

The present invention relates to an electrolytic process of treatment of used piles allowing the recovery of the elements which may undergo beneficiation.

The environmental protection became a major concern. In urban waste, the electrical piles and batteries are recognized like sources of toxic products requiring a particular treatment. Different solutions were already proposed. Thus, the treatment of the batteries to lead and nickel-cadmium is carried out for a long time and led to the recycling of lead and reusable nickel especially in the foundries of the second fusion.

The treatment of the piles is more complex, owing to the fact that their composition and their form are very varied. Several processes were proposed. EP-A-409792 describes a process of simultaneous production of dioxide of manganese and of zinc by electrolysis of the solution obtained while treating by a solvent acid containing of the acid will tétra fluoroboric, of made up such as manganese oxides or zinc, zinc halides or metallic zinc, this process which can be applied with the treatment of used piles having undergone a calcination with 550 DEGREE C in inert atmosphere. JP-60096734 describes a process of treatment for the recovery of elements which may undergo beneficiation starting from used piles, in which the piles are initially crushed, then heated to 500 DEGREE C and then subjected to a chloroammoniacal treatment, then calcined. These processes require however a step of calcination which makes the operations long and expensive.

The purpose of the present invention is providing a process allowing the recovery of elements which may undergo beneficiation starting from used piles, requiring step of calcination and applicable to a nonsorted mixture of piles having different compositions. The process of treatment of used piles of the present invention is a process in which one subjects the used piles to a mechanical treatment in order to dislocate the envelopes of the piles, then with a magnetic sorting in order to separate the ferrous metals, fraction removed from the ferrous metals being then subjected to a flotation in order to eliminate the inert ones, and it is characterized in that:

one subjects the dense inorganic muds obtained after flotation to a leaching by the sulphuric acid;

one adjusts the pH of the solution after obtained leaching with a value ranging between 2,5 and 4 to precipitate sulphate and oxide of mercury and one separates the precipitate obtained;

one réacidifie by sulphuric acid addition the solution obtained after elimination of composed of mercury, then one subjects it to an electrolysis during which zinc settles on cathode and the manganese oxide is formed with the anode.

Preferably, cathode is an aluminium cathode and the anode is selected among the combined lead anodes, the graphite anodes and the anodic titanium anodes.

In the continuation of the text, electrolysis allowing the simultaneous manganese oxide and zinc deposit will be indicated by main electrolysis.

The size of the cell modules most current varies between 70 mm and 5 mm in height and between 30 mms and 5 mms in diameter. In order to optimize the operation of grinding, a device of calibration uninterrupted is preferably placed upstream.

The grinding can be carried out in a mill with toothed discs, preferably cold under a dry draught. It causes the dislocation of the metallic envelope of the piles and the reduction of ferrous sheets to sizes compatible with the subsequent operations.

The load obtained after grinding is washed with water and the solid residues are subjected to a magnetic sorting. A second grinding, carried out on the residues solid resulting from the magnetic sorting allows a finer reduction of these residues, which present an advantage insofar as the granulometry of the load conditions the effectiveness and the duration of leaching and flotation.

The muds removed from the ferrous materials are subjected to a flotation. It allows the separation of the inert ones which are compounds containing carbon black, of the perfluoroalkylsulfonates, plastic and of the paper.

The dense inorganic muds obtained after flotation contain non-ferrous oxides and metals whereas the solution is enriched in electrolyte, mainly in the form of potash, of chloride zinc and ammonium.

Leaching by the sulphuric acid of the dense inorganic muds leads to the putting in solution of the components of the electrodes of the crushed piles. The reaction is enough exothermic and maintains a temperature adapted with the reactional process.

The mercury is eliminated by selective precipitation. To obtain the precipitation of mercury oxides and sulphates, the pH is adjusted with a value between 2,5 and 4, for example by adding of potash.

Main electrolysis is preferably carried out at a less temperature with 100 DEGREE C. Preferably, the temperature lies between 20 DEGREE C and 95 DEGREE C. The bath of main electrolysis is essentially made up by the solution obtained after flotation and elimination of compounds of mercury, which contains zinc sulphate, manganese sulphate, sulphuric acid. The content manganese sulphate of the bath is adjusted between 80 and 320 g/l, the content zinc sulphate between 60 and 400 g/l and the content of sulphuric acid are adjusted between 25 and 40 g/l. The anodic densities vary between 0,7 A/dm² and 2,8 A/dm² and the densities of cathodic current vary between 0,5 A/dm² and 5 A/dm². The outburst of gas accompanying the main reactions to the electrodes and evaporation can be minimized by flotation of a fine layer of paraffin or oil above the bath.

During main electrolysis, zinc is obtained in the form of deposit on cathode; the manganese oxide is obtained in the form of deposit on the anode or powder falling at the bottom of the cell of electrolysis, following the temperature of the bath.

In a mode of putting in work particular of the process of the invention, it is advantageous to add a reducing agent to the electrolysis bath. This reducing agent makes it possible to avoid or limit the manganese oxide formation of the cryptomélane type or phyllomanganate, and consequently to support the manganese oxide obtaining to the lowest degree of the oxidation. The reducing agent can be selected among the boric acid, the formic acid and formaldehyde.

When main electrolysis is carried out after adding of a reducing agent to the electrolysis bath, the process of the invention makes it possible to obtain manganese in metallic form. For this purpose, one after treats by the sulphuric acid manganese oxide obtained with the anode main electrolysis, one optionally adds to the sulphate solution obtained an additive improving the cathodic output such as pyrogallol, the formic acid, formaldehyde, alcohol cyanamillie or the fumaric acid, and one subjects the solution obtained to the one second

electrolysis, during which the manganese metal settles on cathode, whereas the manganese oxide settles poorly on the anode. The material used for cathode is the stellite, and the material used for the anode is selected among lead, graphite or anodic titanium. For the second electrolysis, the content manganese sulphate of the bath is adjusted between 40 and 100 g/l. The bath contains moreover from 10 to 90 g/l of sulphate of ammonia or potassium, and optionally of chloride potassium, added with the mentioned additive improving the faradic output. The pH of the bath is maintained at a value between 5 and 6,5. The density of current varies between 4 mA/cm² and 60 mA/cm². Following the sulphate concentration of the bath, the temperature is attached with a value between 20 DEGREE C and 60 DEGREE C.

This second electrolysis can be carried out in a diaphragm cell.

When the solution subjected to main electrolysis does not contain zinc, the adding with this solution of a reducing agent such as for example the boric acid, the formic acid or the formaldehyde, allows to immediately obtain a metallic manganese deposit on cathode, without the second electrolysis being necessary.

With fine of main electrolysis, the remaining electrolysis bath is rich in sulphuric acid and it can be re-used preferably as solution acid for the step of leaching. This recycling of the bath of main electrolysis on the one hand makes it possible to avoid the reprocessing or the rejection of substantial volumes of effluent acids, and on the other hand makes the process more economic.

Following the nature of the treated piles, the mixture can contain metals such as copper, the nickel or the cadmium, with variable concentrations.

When the mixture of piles contains copper, this one can be recovered by cementing of the solution obtained after leaching.

When the mixture of piles contains nickel and/or cadmium, the nickel and/or the cadmium can be extracted from the solution obtained after main electrolysis, by a selective electrolysis. When the content of nickel and/or cadmium of the solution to be treated is less to 40 g/l, selective electrolysis is carried out in circulation on a loop derived after main electrolysis. If the content of nickel and/or cadmium of the solution to be treated is great to 40 g/l, selective electrolysis is carried out into static.

For selective electrolysis, the potential is maintained between 1,5 V and 5 V, the pH are attached with a value going from 4 to 5,5, the temperature of the bath is preferably maintained between 25 and 50 DEGREE C. Cathode is preferably out of sheet of iron and the anode out of allied lead.

The process of the present invention is illustrated for the following examples which could not limit the invention.

EXAMPLE 1

A mixture of piles having the following composition

cathodic mass 72,8 G (oxides of mn, carbon, KOH)

anodic mass 28,8 G (Zn, KOH, Hg, oxide of Zn)

steel 21,9 G

paper + plastic 7,8 G

anodic stem contact 0,6 G

was crushed in a mill with toothed, cold discs under dry, pendent draught 1 hour. The resulting mass was subjected to a magnetic sorting using a conventional magnetic separator. The fraction removed from the ferrous metals was subjected to a flotation at ambient temperature, under pneumatic agitation. The dense portion was subjected to a leaching by the sulphuric acid with 150 g/l at ambient temperature under mechanical agitation pendent 2 hours. The pH of the solution was adjusted to 3,75 and one precipitate of mercury oxide is formed. The pH of the solution obtained after filtration was adjusted to 2 per sulphuric acid addition. The solution was then subjected to main electrolysis under the following conditions:

MnSO₄ = 110 g/l
ZnSO₄ = 140 g/l
T = 80 DEGREE C
I anodic = 1,2 A/dm² (antimoniated lead anode)
I cathodic = 2,4 A/dm² (aluminium cathode)
Faradic output in MnO₂: 68%
Faradic zinc yield: 80 %

The analysis by X-rays diffraction of the anodic deposit confirms the indexing according to epsilon MnO₂ (ASTM N.30-0820).

EXAMPLE 2

A batch of piles identical with that of example 1 was treated same manner that in example 1 until the elimination of the mercury oxide precipitate. Then, the pH of the solution was adjusted with a value of 2,5, then formic acid was added. The solution was then subjected to main electrolysis under the following conditions:

MnSO₄ = 110 g/l
ZnSO₄ = 140 g/l
T = 80 DEGREE C
I anodic = 1,2 A/dm² (antimoniated lead anode)
I cathodic = 2,4 A/dm² (aluminium cathode)
Faradic output in MnO₂: 25%
Faradic zinc yield: 89 %.

The formed manganese oxide during main electrolysis was redissolved by the sulphuric acid. To the manganese sulphate solution thus obtained, one added potassium sulphate and pyrogallol. The pH of the solution was maintained to 5,8. The composition of the bath was the following one: 50 manganese sulphate g/l, 80 potassium sulphate g/l, 5 ammonium chloride g/l and 0,5 pyrogallol g/l. The conductivity of the bath was 52 ms with 18 DEGREE C and the density of current of 38 mA/cm². A metallic manganese deposit is formed on cathode.

1. Proceeded of processing of used electrical piles for the recovery of the elements which may undergo beneficiation, in which one subjects the used piles to a mechanical treatment in order to dislocate the envelopes of the piles, then to a magnetic sorting in

order to separate the ferrous metals, fraction removed from the ferrous metals being then subjected to a flotation in order to eliminate the inert ones, characterized in that:

one subjects the dense inorganic muds obtained after flotation to a leaching by the sulphuric acid;

one adjusts the pH of the solution after obtained leaching with a value ranging between 2,5 and 4 to precipitate sulphate and oxide of mercury and one separates the precipitate obtained;

one réacidifie by sulphuric acid addition the solution obtained after elimination of composed of mercury, then one subjects it to a main said electrolysis during which zinc settles on cathode and the manganese oxide is formed with the anode.

2. Proceeded according to claim 1, characterized in that one uses for main electrolysis an aluminium cathode.

3. Proceeded according to claim 1, characterized in that one uses for main electrolysis, an anodic titanium or graphite, combined lead anode.

4. Procédé according to claim 1, characterized in that the temperature of putting in work is less to 100 DEGREE C.

5. Proceeded according to claim 4, characterized in that the temperature of putting in work lies between 20 DEGREE C and 95 DEGREE C.

6. Proceeded according to claim 1, characterized in that one adds to the electrolysis bath a reducing agent.

7. Proceeded according to claim 6, characterized in that the reducing agent is selected among the boric acid, the formic acid and formaldehyde.

8. Proceeded according to claim 1, characterized in that one uses for leaching the solution rich in acid obtained with fine from main electrolysis.

9. Proceeded according to claim 1, characterized in that one subjects the piles to a cold grinding under dry draught.

10. Procédé according to claim 1, characterized in that one subjects to a second grinding, front flotation, fraction removed from the ferrous metals.

11. Proceeded according to claim 1, characterized in that one subjects the solution obtained after lixiation to a cementing in order to extract copper, front to adjust the pH for the extraction of composed of mercury.

12. Proceeded according to claim 1, characterized in that one subjects the solution obtained after main electrolysis to a selective electrolysis in order to extract cadmium and/or nickel.

13. Proceeded according to claim 12, characterized in that one carries out selective electrolysis with an attached potential between 1,5 V and 5 V under pneumatic agitation, with a pH between 4 and 5,5, the temperature being maintained between 25 DEGREE C and 50 DEGREE C.

14. Procédé according to claim 12, characterized in that one uses a lead anode combined for selective electrolysis.

15. Proceeded according to claim 12, characterized in that one uses an iron sheet cathode for selective electrolysis.

16. Proceeded according to claim 12, characterized in that selective electrolysis is a static electrolysis.

17. Proceeded according to claim 12, characterized in that selective electrolysis is an electrolysis in circulation on a derived loop.

18. Proceeded according to claim 6, characterized in that one treats by the sulphuric acid the manganese oxide obtained after electrolysis, one adds to the sulphate solution obtained from pyrogallol or of the formic acid and one subjects the solution obtained to the one second electrolysis in a diaphragm cell.

19. Proceeded according to claim 18, characterized in that one uses for the second electrolyses a stellite cathode and a titanium or lead, graphite anode.